the occurrence of the characteristic convulsions, but, after the onset of the symptoms, death usually follows within fifteen to thirty minutes. A *post-mortem* examination of the animal shows a condition of cerebral congestion and thrombosis of the superior longitudinal sinus.

It was considered possible that the narcotic effects produced by the chloroform extract of the resin, and the delirium and convulsions caused by the aqueous extract, as above described, are due to the same substance, and that the difference in the symptoms may depend upon the amount of the poison administered or the rate of its absorption. In order to test this assumption successive sub-toxic doses were given to a small dog during a period of several days. Nothing of a definite nature occurred until the tenth day, when the characteristic delirium commenced, followed shortly by convulsions, and death then ensued within about one hour. The *post-mortem* examination showed a condition of cerebral congestion, and a small patch, apparently of cortical necrosis, near the right crucial sulcus. These experiments thus permit of the following deductions:

(1) That the fruit of *Chailletia toxicaria* contains at least two active principles, one of which causes cerebral depression or narcosis, and the other cerebral excitation, leading to epileptiform convulsions.

(2) That the poison which causes convulsions is very slowly excreted, so that a cumulative effect is produced by the administration of a series of individually innocuous doses.

It may finally be stated that all the physiological experiments required in the course of this investigation were conducted in the Wellcome Physiological Research Laboratories by Mr. H. H. Dale, and our best thanks are due to him for the valuable assistance he has given us.

ON THE ACTION OF ACID CHLORIDES ON MIXTURES OF AMINES.

BY F. B. DAINS.

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IN the course of an investigation on the action of acid chlorides on ureas of the type RNHCSNHR′, the question arose, which an effort was made to answer, whether when a mixture of two amines was treated with an acid chloride, any preference would be shown as to the amine attacked, and if so what the conditions were that would govern it. Thus given a molecular mixture of two amines and an acid chloride, there might be obtained as products, first the acyl derivatives of the two amines plus the hydrochlorides of the two amino bodies, and second the acyl derivative of one amine plus the salt of the other, a condition which can be represented as follows:

$$XNH_2 + YNH_2 + RCOCl = XNHCOR + YNHCOR + XNH_2HCl + YNH_2HCl \text{ or } XNHCOR + YNH_2HCl.$$

The results thus far obtained in this investigation point to the general conclusion, that when there is any appreciable difference in basicity between the two amines, there will be formed largely or altogether the acyl derivative of the more negative amine and the salt of the more positive one.

$$\text{Pos. } NH_2 + \text{Neg. } NH_2 + RCOCl = \text{Neg. } NHCOR + \text{Pos. } NH_2HCl.$$

The terms positive and negative are used in a somewhat restricted sense, referring only to the ease of replacement of the hydrogen atom, since the results from this standpoint may not always agree with those obtained in other ways. Thus from the measurement of the electrical conductivity monoethylamine is a stronger base than ammonia, yet it is found that an amino hydrogen atom of ethylamine is more easily replaced than the hydrogen atom of ammonia.

EXPERIMENTAL.

The experimental work was done under two general conditions, either dissolving molecular quantities of the two amines in a neutral solvent like benzene or ether, and then adding the acid chloride either alone or diluted with the same solvent; or suspending the amines in a relatively large volume of water and then adding the acid chloride as in the usual Baumann-Schotten reaction.

Without making quantitative measurements, it seemed as if the reaction proceeded more rapidly and smoothly under these conditions than when caustic soda was used to combine with the hydrochloric acid set free. In the majority of cases the hard granular acyl derivative formed almost immediately, while the hydrochloride of the amine remained in solution when water was used.

Ammonia and Primary Amines.—Ammonia, if not in too great excess, can be used to combine with the free acid in the formation of benzoyl derivatives of primary amines giving a smooth and rapid reaction.

Ammonia and Ethylamine.—One molecule of ammonia and one molecule of monoethylamine were dissolved in an excess of water and one molecule of benzoyl chloride added with shaking. An oil was formed which was very soluble in alcohol and which, on standing, slowly solidified to long needles of ethylbenzamide (melting-point 67°). The solution contained ammonium chloride.

Ammonia and Aniline.—Benzoyl chloride gave, with molecular proportions of ammonia and aniline, a hard granular precipitate of benzanilide, and ammonium chloride.

Ammonia and o-Toluidine.—These amines gave, in water solution with benzoyl chloride, easily and smoothly *o*-benztoluide and ammonium chloride.

Ammonia and m-Brom-p-toluidine yielded under the above conditions ammonium chloride and benzoic *m*-brom-*p*-toluide.

Ammonia and Phenylhydrazine.—Benzoyl chloride was added to the above amines in water solution. The substances reacted quickly and on examining the products formed, there were discovered ammonium chloride, phenylhydrazine, and dibenzoylphenylhydrazine. The course of the reaction can be represented as follows:

$$2NH_3 + 2C_6H_5NHNH_2 + C_6H_5COCl = 2NH_4Cl + C_6H_5NHNH_2 + \\ C_6H_5N(COC_6H_5)NHCOC_6H_5.$$

The first action of the acid chloride is to form the monobenzoylphenylhydrazine, but as this has still a second replaceable hydrogen atom and is more negative than either the ammonia or the phenylhydrazine, this hydrogen atom is substituted by the second benzoyl group giving the dibenzoylphenylhydrazine.

Aniline and Other Primary Amines.—Aniline, the simplest of the aromatic amines, affords a convenient standard of comparison in its reactivity with other amino bodies as to their relative positive or negative nature. Thus, where the second amine is more positive the products are an acyl anilide and the salt of the second amine. This has already been shown to be the case with ammonia and aniline.

Aniline and Ethylamine. — With molecular proportions of ammonia, ethylamine and benzoyl chloride in water solution, the products were ethylamine hydrochloride and benzanilide.

Aniline and o-Toluidine.—Acetyl chloride gave with these substances in benzene solution acetanilide and a precipitate of *o*-toluidine hydrochloride. When acetic anhydride was added to a molecular mixture of aniline and the toluidine, the reaction product yielded, on investigation, acetanilide and *o*-toluidine, a result wholly in accordance with the action of the acetyl chloride.

When succinyl chloride was added to the aniline and *o*-toluidine suspended in water, the solid product formed consisted only of succinanilide; no trace of succintoluide was discovered, a result which corresponds to the action of the more simple acid chlorides.

These same two amines in benzene solution gave with benzoyl chloride mainly benzanilide and *o*-toluidine hydrochloride, while small amounts of *o*-benztoluide and aniline were also identified.

Aniline and p-Toluidine.—When acetyl chloride is added to a solution of aniline and *p*-toluidine in benzene, much heat is evolved and the solution contains acetanilide and the hydrochloride of *p*-toluidine.

Aniline and Pseudocumidine yield with acetyl chloride in benzene solution acetanilide and pseudocumidine hydrochloride.

Aniline and Phenylhydrazine. — The aniline and phenylhydrazine were suspended in water and benzoyl chloride added. The results were entirely in harmony with the preceding, benzanilide and the salt of phenylhydrazine being formed.

The second series of amines includes those that are more negative than aniline, giving as general products, more or less completely, aniline hydrochloride and the acyl derivative of the second amine.

Aniline and m-Nitroaniline were suspended in a large excess of water and benzoyl chloride added. The solid product proved to be the benzoyl derivative of *m*-nitroaniline, while the filtrate contained aniline hydrochloride and a little *m*-nitroaniline.

In benzene solution these amines gave mainly *m*-nitroacetanilide and the hydrochloride of aniline.

Aniline and p-Bromaniline.—In benzene solution the chief products with benzoyl chloride were *p*-brombenzanilide and aniline hydrochloride. A little *p*-bromaniline and traces of benzanilide were also isolated.

Aniline and m-Brom-p-toluidine. — The amines suspended in water yielded with benzoyl chloride benzoic *m*-brom-*p*-toluide, and aniline hydrochloride.

Aniline and o-Anisidine.—Benzoyl chloride gave with the above as main products aniline hydrochloride and the benzoyl derivative of *o*-anisidine. A little benzanilide was also isolated.

Aniline and p-Phenetidine.—These give, either in water or benzene solution, mixtures of products, with the benzoyl-*p*-phenetidide predominating.

Aniline and m-Xylidine.—Like the preceding, aniline and *m*-xylidine tend to give with benzoyl chloride, when suspended in water, a mixture of products. The benzoyl-*m*-xylide, however, is in excess, while the filtrate contains the salts of aniline and some *m*-xylidine.

In comparison with aniline, a much greater proportion of the acyl *m*-xylide is obtained than with other methyl derivatives like *o*- and *p*-toluidines, and pseudocumidine, which are more positive to aniline.

Aniline and α-Naphthylamine.—These amines in benzene solution give with acetyl chloride chiefly α-acetnaphthalide and aniline hydrochloride, while in water solution with benzoyl chloride, there are obtained largely benzoic α-naphthalide and the aniline salt.

Aniline and β-Naphthylamine.—Acetyl chloride gave with these amines in benzene solution primarily acet-β-naphthalide and aniline hydrochloride, together with some β-naphthylamine.

o- and p-Toluidine.—In one experiment in ether solution with acetyl chloride *p*-acettoluide and *o*-toluidine were obtained, but in another case with benzoyl chloride a mixture of the two benztoluides resulted. The effect of the *o*-, *m*- and *p*-positions on the reaction will be investigated further.

Pseudocumidine and m-Xylidine.—These bodies when dissolved in benzene and treated with benzoyl chloride yielded the hydrochloride of pseudocumidine and benz-*m*-xylide, a result in accordance with their relative action toward aniline.

Aniline and Monomethylaniline.—Benzoyl chloride in water solution gave with these substances aniline hydrochloride, benzanilide, and an oily product which possibly contains some benzoyl-monomethylaniline, but it has not as yet been obtained in a pure enough state for identification.

Aniline and Diphenylamine.—Molecular quantities of these amines yield in benzene solution benzanilide, aniline hydrochloride, diphenylamine and unchanged benzoyl chloride.

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PIPERONAL AND HYDROGEN CHLORIDE: A TWO-COMPONENT THREE-PHASE SYSTEM.

BY F. J. MOORE.

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SINCE it appears from a recent paper by D. McIntosh,[1] that he is also studying the action of the halogen acids upon aldehydes, the following extremely incomplete observations are communicated at this time to avoid any possibility of collision.

While investigating the action of some organic compounds upon piperonal, the accidental observation was made that this substance liquefies when brought into contact with dry hydrogen chloride. When the liquid thus formed was exposed to the air on a watch-glass, crystals appeared. A melting-point determination showed that these consisted of piperonal. The explanation of these phenomena obviously is, that piperonal adds hydrogen chloride as long as the pressure of the latter upon its surface is about one atmosphere, but the vapor pressure of the product is so great that when the partial pressure of the hydrogen chloride falls, all the gas is liberated. In order to bring out these relations more clearly, the apparatus was devised which is represented in the accompanying diagram.

B is a small bulb about 35 mm. high and 7 in diameter—outside measurement. D is a much larger cylinder about 135 mm. long and 40 in diameter. E is a leveling-bulb connected with D by thick-walled rubber tubing.

Somewhat less than a gram of piperonal is first introduced into B. The most convenient way to do this is to melt some piperonal, and draw it in through A by suction. Mercury is next poured into the bulb E, and the latter is raised until the mercury fills D and reaches the point x, just leaving the tube C open. Meanwhile the piperonal in B is kept melted by means of a beaker of

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[1] This Journal, 28, 588 (1906).